B.Tech Project Report on

Study of chemical leaching of aluminium from red mud

For partial fulfillment of the requirements for the degree of

Bachelor of Technology
in
Chemical Engineering

SUBMITTED BY

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CERTIFICATE

This is to certify that the report on the Project entitled '**Study of chemical leaching of aluminium from red mud'** is a bonafide record of the work carried out by Abhilekh Behera (111CH0388) under my supervision and guidance towards the partial fulfillment of requirement for the award of the degree of Bachelor of Technology in Chemical Engineering at National Institute of Technology, Rourkela. To the best of my knowledge, the matter embodied in this thesis has not been submitted to any other university or institute for the award of any degree.

Place: Rourkela, Odisha
Date: 06th May, 2015

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In pursuit of this academic endeavor, I feel that I have been singularly fortunate; inspiration, guidance, direction, cooperation, love and care, all came my way in abundance and it seems almost an impossible task for me to acknowledge the same in adequate terms.

Yes, I shall be failing in my duty if I do not record my profound sense of indebtedness and heartfelt gratitude to my supervisor Dr. (Mrs.) Susmita Mishra who guided and inspired me in pursuance of this work. Her association will remain a beacon of light to me throughout my life.

I owe a depth of gratitude to Prof. P Rath, H.O.D, Department of Chemical Engineering, for all the facilities provided during the course of my tenure. I thank for the support, encouragement and good wishes of my parents and family members, without which I would not have been able to complete my report.

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ABSTRACT

In this project work red mud was utilized for study of aluminium extraction using acid leachates. Both organic and inorganic acids were used in the chemical leaching experiments. Sulphuric acid, Citric acid and Oxalic acid were used for leaching individually or in combined form with different ratios. High quantities of red mud is generated by alumina industries as a waste product which is generally stockpiled in open area leading to soil, air and water pollution because of its caustic nature. Red mud sample was collected from Vedanta Alumina Ltd, lanjhigarh (Odisha) and various constituents were analysed. Since aluminium is present nearly 8 % in the red mud , so if economically viable process is used to extract the aluminium then the extracted aluminium can further be used in the alumina industries. From observation it was seen that highest percentage of aluminium was solubilised with acid mixtures of citric acid and oxalic acid taken together in 2:1 ratio. Further it was found out that the extraction is better in the room temperature and low pH.

INTRODUCTION

Red mud is a reddish brown colour solid waste product produced from alumina industries.

The Bayer's process is mainly used in these industries for the digestion of the bauxite ore in concentrated sodium hydroxide (NaOH) to form soluble sodium aluminate leaving red mud as a waste. 0.8 - 1.5 tonnes of red mud is produced per tonne of alumina produced. 900 lakh huge amounts of red mud is delivered consistently globally . Red mud is highly alkaline in nature having pH 11 – 13 and it mainly contains Fe_2O_3 , Al_2O_3 , SiO_2 and TiO_2 .

Red mud delivered from the industries are for the most part stockpilled in open yard which prompts significant issues in soil,air & water which leads to exceedingly pollution in nature and environment.

The disposal of red mud is now a major headache for the government for which researchers are currently working to develop suitable methods by which it can be utilised effectively.

In the recent years great efforts have been made to use red mud directly in multiple fields of environmental protection such as gas purifying, water treatment or soil improvement and in production of building materials such as cement,glass etc. Catalyst is another field where red is used. But these methods usually suffer new contamination or difficulty in further treatments and economic value produced is very low.

Inspiration for the project

The cost for transportation and pollution decrease are the serious problem faced by the alumina industries in dumping the red mud after its formation. Since major part of the red mud contains Fe_2O_3 & Al_2O_3 (almost 60 %) and many other metals, so red mud is a potential source of many metals. Red mud is used in the cement industry for the manufacture of cement bricks , but those applications can utilize only few amount of red mud produced over the year. Moreover those application further leads to air and soil pollution. Until now, red mud has found limited commercial utilization in road making Portland cement. So in this project I am studying the extraction of aluminium from red mud using chemical leaching. So that the extracted aluminium can again be used in alumina production.

LITERATURE REVIEW:

Bauxite ore refers to the ore containing high amount of aluminium oxide (Al_2O_3) and low amount of hematite (FeO_3) and silica and other oxides . Bauxite composition make the ore to mine from various place and extract aluminium from it economically. Other rich sources of aluminium include a variety of rocks and minerals which includes aluminium phosphate rock, aluminous shale and slate and Kaolites (high alumina clays), etc.. Although, bauxite is found worldwide. The countries with the largest economically mineable deposits, in order of production are India , Australia ,Jamaica, Brazil & Guinea.

Bayer's process overview

Bayer process is an economical solution for producing aluminium oxides from bauxite ore using concentrated NaOH solution (caustic soda) at high temperature and pressure . In 1887, Bayer figured out accidentally that the aluminium hydroxide, precipitated from alkaline solution was crystalline and could easily washed and filtered . The NaOH selectively dissolves Al_2O_3 from bauxite ore ; this produces sodium –aluminate . Then, $Al(OH)_3$ precipitation is done, which is than further calcined to produce Al_2O_3 , from which metal is recovered. The Bayer process is capable of producing huge quantities Al_2O_3 and aluminium hydroxide with high – purity aluminium at relatively low – cost. This in fact created opportunity for marketing profitability . The Bayer process is the principal industrial method of refining bauxite to produce alumina. Bauxite is the most important ore of aluminium. It contains only 30-54% alumina , Al_2O_3. The rest is a mixture of silica, various iron oxides, and titanium dioxide, zinc and phosphorus ,vanadium and nickel etc. are found in trace amount. The alumina must be purified before it can be refined to aluminium.

$$Al_2O_3 + 2\ NaOH \rightarrow 2NaAlO_2 + H_2O$$

A large amount of the alumina produced is then subsequently smelted, in order to produce aluminium. Metallic aluminium is very reactive with atmospheric oxygen. A thin layer of alumina quickly forms on any exposed aluminium surface. This layer protects the metal from further oxidation due to its nature. Through anodizing thickness and properties of this oxide layer can be enhanced. A number of alloys, such as aluminium, magnalum, bronzes are done to increase corrosion resistance of the materials. One metal whose growth in the past century has been very fast is aluminium. Its strength and light weight guarantees its demand, especially in transportation where fuel efficiency is of great importance.

Annual world production of alumina is approximately 450 lakh tons, over 90% of which is used in the manufacture of aluminium metal. Due to high melting point Al_2O_3 is used as a refractory material. The major uses of aluminium oxides are in refractory, ceramics , polishing, and abrasive applications.

An aluminium oxide is an electrical insulator, but still has a relatively high thermal conductivity. Red Mud is a by-product of the Bayer process . Its is red in colour due to presence of iron oxides. The amount of red mud generated, per ton of alumina produced varies greatly. It depends on the type of bauxite used i.e. from 0.3 tons for high grade bauxite to 2.5 tons for very low grade. The chemical and physical properties of red mud depends primarily on the bauxite used and to a lesser extent the manner in which it is processed. The main solid waste product of alumina industry is Red mud.

Ore preparation and Mineral processing:

To facilitate efficient digestion, at this stage, a function of providing a continuous, consistent and appropriately charged feed to the digesters in the Bayer process is done. Generally, the ore is washed first and and irrelevant contaminants such as dirts are removed using screen. This procedure is usually completed at the mine itself. Particle size is regulated/ fixed in the same location where the rest of the Bayer process takes place. A great number of plants now utilize wet grinding mills. Wet grinding mills are charged with the bauxite ore and a portion of the process solution in order to make slurry. To return the oversize particles to the mill for further grinding screens and hydro cyclones are used. To utilize abrasion and finalize particle size reduction Research has been done on the effects of holding the ground slurry for extended time periods in mechanically agitated tanks.

Background of Red mud:

Extensive research was done approximately two decades ago and further. At that time researcher's aim was on the recovery of iron and aluminium . Attempts were also made to develop a safe material from red mud that could be used for building materials. One reason for this lack of current research is that research has moved away from iron and aluminium recycling to things of more values such as precious metals such gold and rare earth element extraction such as platinum.

Because, the modern high grade deposits of the Bauxite ore are not available in developed countries, they are now being mined in developing countries such as India, China, Papua, Yugoslavia, Russia and New Guinea. These countries are not as conscious about the environment and thus there is no push for public research to continue.

This research is primarily focusing on the extraction of rare earth element as well as the development of construction material from red mud.

Application of red mud has been tried in limited scenario, as a constituent in industrial construction aggregates, road surface material, such as bricks, and cement with other waste products such as fly ash. It has also been tried as a soil modifier and air purifier .

Space requirements for storage of red mud are one of the largest constant problems facing the aluminium industry to date. There are two current methods of storage. The first is to simply pump the red mud into holding ponds. However, this method takes up a considerable amount of land. The other way to store the mud is to first dry it and then dry stack it. Once there is sufficient red mud the dry stack is then covered with topsoil. This method still alleviates some of the issue of land use however; the land cannot be used for farming or to live on. Farming cannot occur due to the fact that red mud is extremely basic in chemical, nature due to the large amounts of sodium used in the original processing of aluminium that is left in the by-products. Although there have not been any reports of leaching from the red mud through the liners there is still the risk of caustic soda leaching into groundwater. Another risk is leaching of heavy metal into the groundwater such as lead, cadmium and mercury.

Digestion of bauxite:

1) Selective dissolution of alumina from ore.

(e) Grinding: bauxite ore is finely grinded by ball mill to size < 150mm by two numbers of toothed double roll crushers also called as primary crusher to enhance better contact during digestion.The crushed bauxite is then transferred to the aluina plant using cable belt. The speciality of the cable belt is that is that it not only has vertical curves like conventional belts but have several horizontal turnings to meet the requirement of the hilly terrain. Then recycled caustic soda solution is added to produce a slurry suitable for pumping and lime is added for phosphate control and mud recovery.

(f) Desilication: The silica present in the bauxite in the form of kaolinite is called reactive silica, since it react with NaOH easily to form sodium silicate. This sodium silicate deposits as scale on the wall of the vessels and heat exchanger resulting in reduced process efficiency. So harmful reactive are converted to sodium aluminate silicate or sodalite which is a stable compound.

(g) Digestion: The fine bauxite slurry in caustic soda solution is heated in tanks to achieve 105 ˚C. Sodium hydroxide reacts with alumina tri hydrate to form sodium meta aluminate. The non-reactive components such as iron oxide, bohemite and silicon dioxide remain in suspended form in the slurry. Supply steam for heating the slurry is at 9 bar and 210 ˚C.

The chemical reactions can be given as:

$$2NaOH + Al_2O_3 . 3H_2O \rightarrow 2NaAlO_2 + 4H_2O$$
$$2NaOH + Al_2O_3 . H_2O \rightarrow 2NaAlO_2 + 2H_2O$$

(2) Sand separation : Digested slurry having about 100 gm/lit solid is fed tangentally to small conical flasks called cyclones. Due to tangential feeding, the particles experience centrifugal force and are thrown towards periphery and collide on the wall of the cyclone. Heavier particles then fall under gravity and get separated from bottom. The slurry having very small particles come out from the top of the cyclone and come out from top of the cyclone and come to a tank called dilution tank. The separated sand is washed with water extract soda from it and the washed liquor is fed to the top of dilution tank. The slurry here also contain solid and separated in subsequent stages and washed with water for soda recovery.

(a) Settlers : these are big tanks having dia of more than 30 m and height 6 m. Desilicated slurry is fed at the centre and the mud settles down and clear liquor remains at the top. Slow speed rake mechanism drives the settled mud from the centre to periphery. Synthetic flocculant is dosed to the settler feed to enhance rate of settling. Settler overflow containing about 400 mg/ lit of solid and 165 gm/lit soda is collected in an overflow tank.

(b) Security filtration : since 400 mg/lit of solid impurity in the liquor will make the alumina impure in precipitation upto unaccepted limit, further separation of solidis done by means of filtration. For this purpose, settler overflow liquid is filtered in security filter or Kelly filter to bring down the solid from 400 mg/lit to below 30 mg/lit. Kelly filters are pressure leaf filters being operated at 3 ata pressure. Quick lime solution is used as filter aid to help in filtration. The liquor there afteris called as aluminate liquor and is ready for alumina production by precipitation.

(3) Precipitation

Aluminate liquor is cooled down to about 65 ˚C in a plate heat exchanger to achieve better precipitation. As per quality demand of precipitated products grain size is most significant and in order to achieve bigger particles, small hydrate particles are mixed with aluminate liquor so that alumina hydrate precipitation takes place on those particles and their size increases. At the end of precipitation process , the particles are classified as per the size and coarse particles are taken out as final product hydrated alumina. The fine particles are mixed with fresh aluminate liquor to allow precipitation on the surface to make them grow further. In this manner the coarse particles are taken out and fine particles are recycled to precipitator after mixing with aluminate liquor. After removal, the mother liquor is called spent liquor. The fine particles slurry is filtered in seed filters to separate the mother liquor called as spent liquor. The spent liquor received from both product and seed filters is heated up in the plate heat exchangers while cooling aluminate liquor and dispatched to evaporation area.

The seed hydrate is not only put in aluminate liquor for particle growth but also for increasing the rate of precipitation as auto precipitation rate of aluminate liquor is very low. Low concentration of soda in aluminate liquor , low precipitation temperature, high surface area of seed hydrates, high amount of seed hydrates are favouring factors for better precipitation. Aluminate liquor mixed with seed is kept in precipitators for about 40 hrs to achieve substantial production. There are 16 precipitators of 4200 m^3 effective volume each in each stream.

(a) Evaporation : the spent liquor at 80 ˚C is stored in spent liquor tanks. Part of the liquor is pumped to ball mill to help in wet grinding and predesilication. Major portion of liquor is concentrated in evaporators and used for digestion. The steam condensate from multiple effect evaporators is sent back to steam plant. Generated vapour is condensed in different effect and the condensate is used in different area as sodic condensate. To enhance capacity of evaporation batter, the last effect is operated under vacuum and the vacuum is generated by spraying cooling water to the generated vapour. The product of evaporation battery is called green liquor as it is capable of giving production, the temperature is 105 ˚C and concentration is 225 gpl.

The cooled pregnant liquor flows to rows of precipitation tanks which are seeded with previously Precipitated crystalline tri-hydrate alumina. Usually they are of an intermediate or fine particle size to assist crystal growth. The correct particle size is important to smelter operations. So, sizing is carefully controlled. The finished mix of crystal sizes is settled from the liquor stream and separated into their size ranges "gravity" classification tanks.

Caustic liquor which is essentially free from solids overflows from the tertiary classifiers and then it is returned through an evaporation stage where it is re-concentrated, heated and recycled to dissolve more alumina in the digesters. Fresh caustic soda is added to the stream to make up for process losses.

(4) Calcinations of alumina:

The hydrated alumina received from precipitation is washed in drum filters to reduce impregnated soda. In order to remove bound or chemically combined moisture i.e. $3H_2O$ from the hydrate it is subjected to temperature of 1000 ˚C furnace. The temperature is achieved by burning fuel oil with air. There are three fluid bed calciners which have rated capacity of 5500 tons of alumina/day.

$$2Al(OH)_3 + \text{heat} \rightarrow Al_2O_3 + 3H_2O$$

The largest manufactures in the world of alumina are ALCAN, ALCOA, RUCAL, NALCO, Queensland Alumina Limited (QAL) etc.

An aluminum oxide is an electrical insulator, but still has a relatively high thermal conductivity.

The is α-Al_2O_3 called corundum, most commonly occurring crystal line alumina. Its hardness makes it suitable for use as an abrasive and also as a component in cutting tools. Bauxite residue (also known as "red mud") is a by-product of the Bayer process.

1.1Table of Wt % of elements in red mud.

Sl no	Elements	Wt %
1	Iron (Fe)	36-39
2	Aluminium(Al)	7-11
3	Calcium (Ca)	5-10
4	Titanium (Ti)	3-6
5	Silicon(Si)	1-3

The leaching of Red Mud with organic and inorganic acids is studied and literature shows that aluminium solubilisation increase with the mixture of both organic and inorganic acids. However if the rate of solubilisation and the concentration of solubilisation can be increased, then the extraction process can be more economical and can be used in wide areas and the red mud can be utilized and stockpilation can be reduced.

3 - MATERIALS AND METHOD

3.1 Materials used:

a) Red mud obtained from Vedanta Alumina Ltd Lanjigarh,Odisha.

3.2 Chemicals used :

a) Sulphuric acid (12 N)
b) Citric acid (1.25 N)
c) Oxalic acid (0.75 N)

Red mud was taken from Vedanta Alumina Ltd. Lanjigarh, Odisha. The chemical analysis of red mud was done by XRD analysis. The composition of red mud is given in the table below.

Sl no	Compound	Wt %
1	Fe_2O_3	48.2
2	Al_2O_3	7.3
3	SiO_2	8.0
4	TiO_2	1.4
5	CaO	0.9

3.3 - Red Mud characterization

Moisture content :

Wt. of the crucible used : 2 gms

Wt of the sample(with crucible) before kept in oven =40.1 gms

The sample was kept in the hot air oven at 110 °C for 90 mins.

Wt of the sample with crucible = 37.48 gms

Moisture content = (Initial wt. – dried wt.)/Initial wt. * 100 = [(40.1 – 37.48)/ 40.1] * 100 = 6.53 %

3.4 Main objective:

Our objective is to leach red mud using various acids (sulphuric acid , citric acid and oxalic acid) and study the solubilisation concentration of aluminium at different pH and temperature. The acids were then combined at different ratios and the solubilisation is tested.

Effect of contact time on Aluminium leaching using individual acids.

THEORY: In this experiment, the aluminium concentration was studied with different acids such sulphuric acid , citric acid , oxalic acid taken separately with respect to the time taken for maximum solubilisation of aluminium taking the pH constant.

- 25 grams of fine red mud was taken in an Erlenmeyer flask.
- 150 ml of deionised water was added to it.
- Sulphuric acid was added to it until the pH changes to 2
  .
- pH was measured using the pH meter.
- Similar experiment was repeated using citric acid and oxalic acid.
- All the samples were brought to the final volume of 200ml.
- The three samples were kept in the orbital shaker incubator for 1 hour for leaching at 28 ˚C & 200 rpm.
- The samples were collected and taken for atomic absorption spectroscopy analysis to civil department.
- Aluminium solubilisation was studied with the help of AAS.

Effect of pH on Aluminium Leaching

Theory: In this experiment the samples were taken with different pH taking the stirring rate (200 rpm) and time(24 hrs) constant.

- 25 grams of fine red mud was taken in an Erlenmeyer flask.
- 150 ml of deionised water was added to it.
- Sulphuric acid was added to it until the pH changes to 1.
- pH was measured using pH meter.
- The experiment was repeated for different pH.
- Again steps were repeated for citric acid and oxalic acid.
- Samples of different pH were taken.
- The samples were kept in the shaker for 24 hours for leaching at 28 ˚C & 200 rpm.

- The samples were collected and taken for atomic absorption spectroscopy analysis to civil dept. Aluminium solubilisation was studied with the help of AAS.

Effect of acid ratio on aluminium leaching

Theory: In this experiment the samples were taken with combined acid mixtures (2:2) at different pH and the aluminium concentration was studied.

- 25 grams of fine red mud was taken in an Erlenmeyer flask.
- 100 ml of deionised water was added to it.
- 20 ml of sulphuric acid and 20 ml of citric acid were added to the flask.
- pH of the mixture was adjusted with the oxalic acid.
- The final volume was adjusted to 200 ml .
- Samples of different pH were taken .

- The experiment was repeated for 20ml sulphuric acid and 20 ml oxalic acid with citric acid used for pH control.

- Similarly it was conducted for 20ml oxalic acid and 20ml citric acid with sulphuric acid used for pH control.

- All the samples were taken for leaching for 24 hours at 28 ˚C & 200 rpm in the shaker.
- The samples were collected and taken for atomic absorption spectroscopy analysis to civil dept.
- Aluminium solubilisation was studied with the help of AAS.

Effect of combined mixture of citric acid and oxalic acid with different pH

Theory: In this experiment the samples of combined ratio of oxalic acid and citric acid were taken with different pH and aluminium solubilisation was studied.

- 25 grams of fine red mud was taken in an Erlenmeyer flask.
- 100 ml of deionised water was added to it.
- 20 ml of citric acid and 10 ml of oxalic acid were added to the flask.
- pH of the mixture was adjusted with the sulphuric acid.
- The final volume was adjusted to 200 ml.
- Samples of different pH were taken with fixed amount of citric acid and oxalic acid.
- Similar steps were repeated for 10ml citric acid and 20ml oxalic acid.
- All the samples were taken for leaching for 24 hours at 28 ˚C & 200 rpm in the shaker.
- The samples were collected and taken for atomic absorption spectroscopy analysis to civil dept.
- Aluminium solubilisation was studied with the help of AAS.

Effect of combined ratio (2:1) acid mixture of citric acid and oxalic acid taken together at different pH

Theory: In this experiment the samples were taken with combined acid mixtures (2:1) ratio with different pH and the aluminium concentration was studied.

- 25 grams of fine red mud was taken in an Erlenmeyer flask.
- 100 ml of deionised water was added to it.
- 20 ml of oxalic acid and 10 ml of citric acid were added to the flask.
- pH (=3) of the mixture was adjusted with the sulphuric acid.
- The final volume was adjusted to 200 ml.
- the experiment was repeated for 20ml citric acid and 20 ml oxalic acid with sulphuric acid used for pH control.
- Similarly it was conducted for 10ml oxalic acid and 20ml citric acid with sulphuric acid used for pH control.
- All samples were adjusted to 200 ml and pH to 3.
- All the samples were taken for leaching for 24 hours at 28 ˚C & 200 rpm in the shaker.
- The samples were collected and taken for atomic absorption spectroscopy analysis to civil dept.
- Aluminium solubilisation was studied with the help of AAS.

Effect of stirring rate on the Aluminium solubilisation at different pH

Theory: In this experiment we are studying the effect of stirring rate for the solubilisation of aluminium in the acid leachate.

- 25 grams of fine red mud was taken in an Erlenmeyer flask.
- 100 ml of deionised water was added to it.
- 20 ml of citric acid and 10 ml of oxalic acid were added to the flask.
- pH of the mixture was adjusted with the sulphuric acid.
- Samples of different pH were taken.
- The final volume was adjusted to 200 ml using deionised water .
- The samples were taken for leaching for 24 hours with 28 ˚C but for different stirring rate in the shaker.
- The samples were collected and taken for atomic absorption spectroscopy analysis to civil dept.
- Aluminium solubilisation was studied with the help of AAS.

Effect of temperature on aluminium solubilisation.

Theory: In this experiment we are studying the effect of temperate for the solubilisation of aluminium in the acids leachate.

- 25 grams of fine red mud was taken in an Erlenmeyer flask.
- 100 ml of deionised water was added to it.
- 20 ml of citric acid and 10 ml of oxalic acid were added to the flask.
- pH of the mixture was adjusted with the sulphuric acid.
- Samples of different pH were taken.
- The final volume was adjusted to 200 ml using deionised water .
- The samples were taken for leaching for 24 hours with stirring rate of 200 rpm.
- Different temperatures were taken for each samples.

- The samples were collected and taken for atomic absorption spectroscopy analysis to civil dept.

- Aluminium solubilisation was studied with the help of AAS.

4 – RESULT AND DISCUSSION

Table 1 – Effect of individual acids at different contact time.

Time (in hours)	With Citric acid	With Oxalic acid	With Sulphuric acid
1	4340	4410	389
3	4347	4477	524
6	5608	7700	1453
9	5690	9031	1725
12	5741	6910	1967
18	5749	6931	1983
24	5756	6938	1932

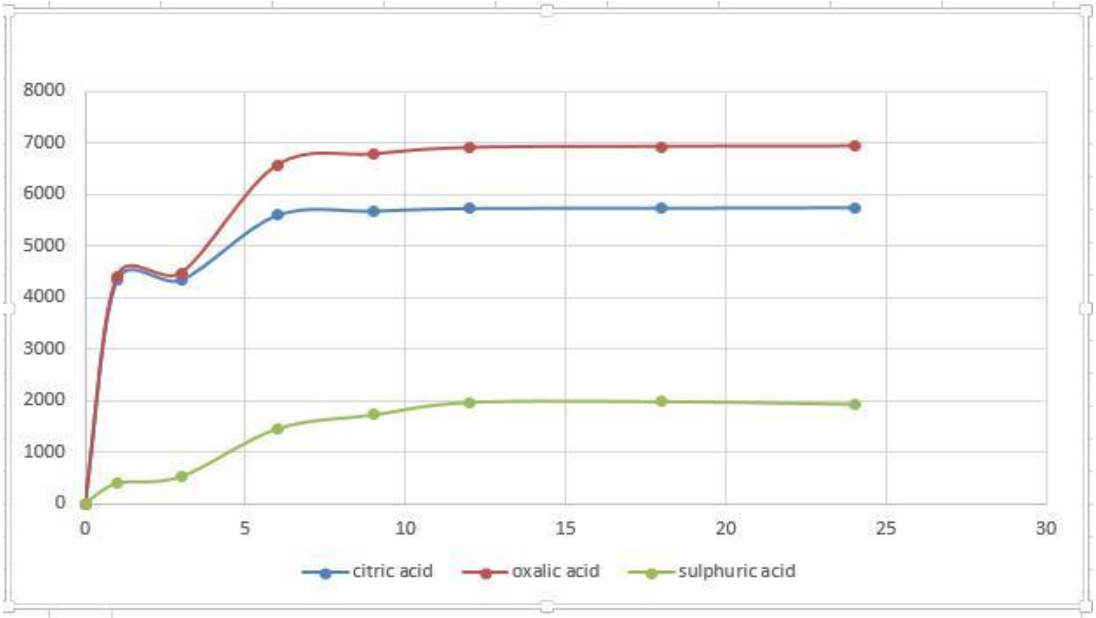

Figure 1 : Influence of contact time on Al leaching

Due to increase in contact time the aluminium leaching increases which is more rapid during the 1st hour for citric acid and oxalic acid. Maximum leaching of 9031 mg/litres was obtained for oxalic acid within 9 hrs. the leaching action was less for H2SO4 compared to oxalic acid and citric acid due to chelation effect of organic acids that improves the rate of leaching.

Table 2 Effect of pH on Al solubilisation with Sulphuric acid.

pH	With Suphuric acid
1	842
2.1	729
3	127
4	0
5	0

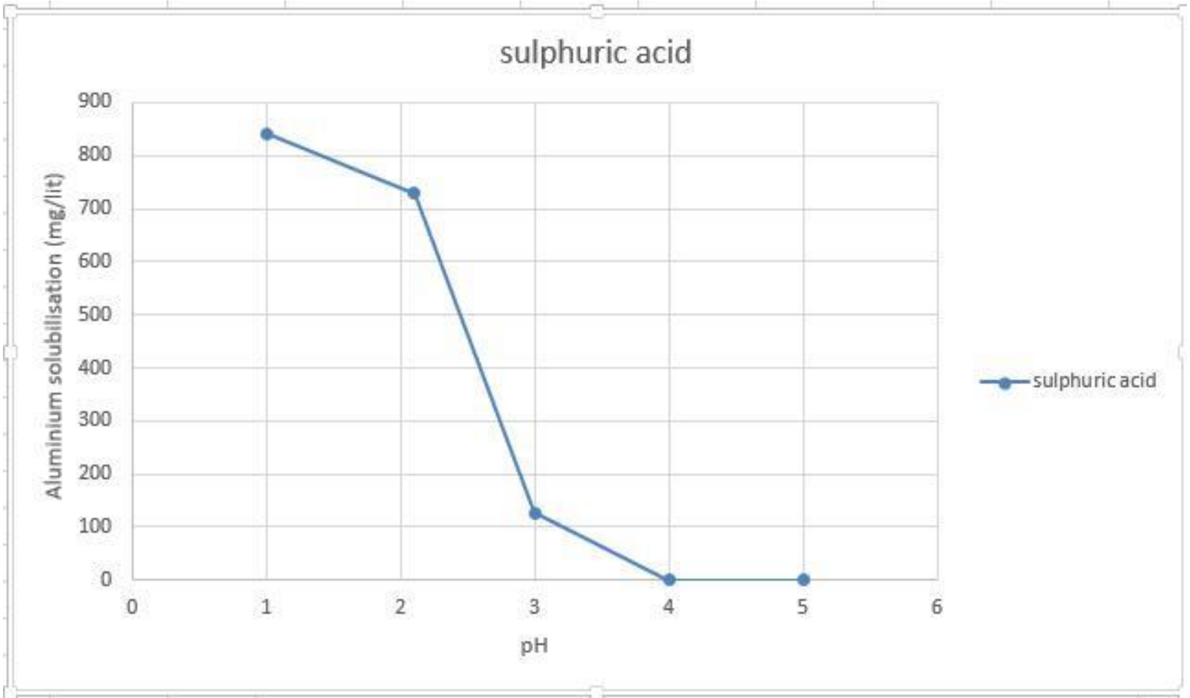

Figure – 2 influence of pH on Al solibulisation by sulphuric acid.

pH has maximum influence on leaching of aluminium using sulphuric acid which was evident from figure 2. Leaching amount decreased with increasing pH. However maximum concentration was achieved during pH 2 and 3. Hence leaching of Al using sulphuric acid was prominent and maximum 842 mg/lit could be achieved at acidic pH 1. At lower pH acids are being progressively protonated which leads to increase in leaching.

Table – 3 Effect of pH on Al solibulisation by citric acid :

pH	With citric acid
2.1	4200
4.3	2768
5	2176
7	139
9	110
11	91

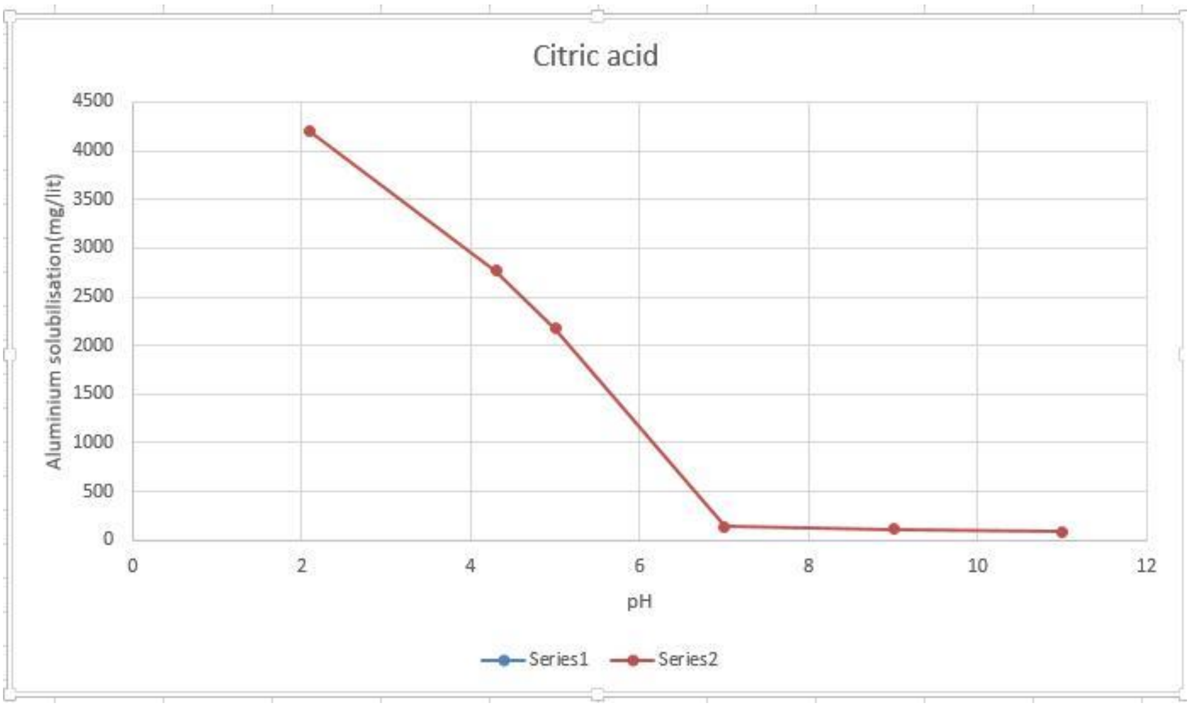

Figure 3: influence of pH on Al solubilisation by citric acid

Using citric acid maximum 4200 mg/lit of Al could be leached at pH 2.1 . However at pH < 2 and >2 leaching amount decreased till at pH 7 where very less solubilisation occurred. At higher pH >7 solubilisation of Aluminium was reduced due to less release of H^+ ions.

Table 4 - Effect of pH on Al solubilisation by oxalic acid

pH	Oxalic acid
3	7763
5	4132
7	1330
9	562
11.2	489

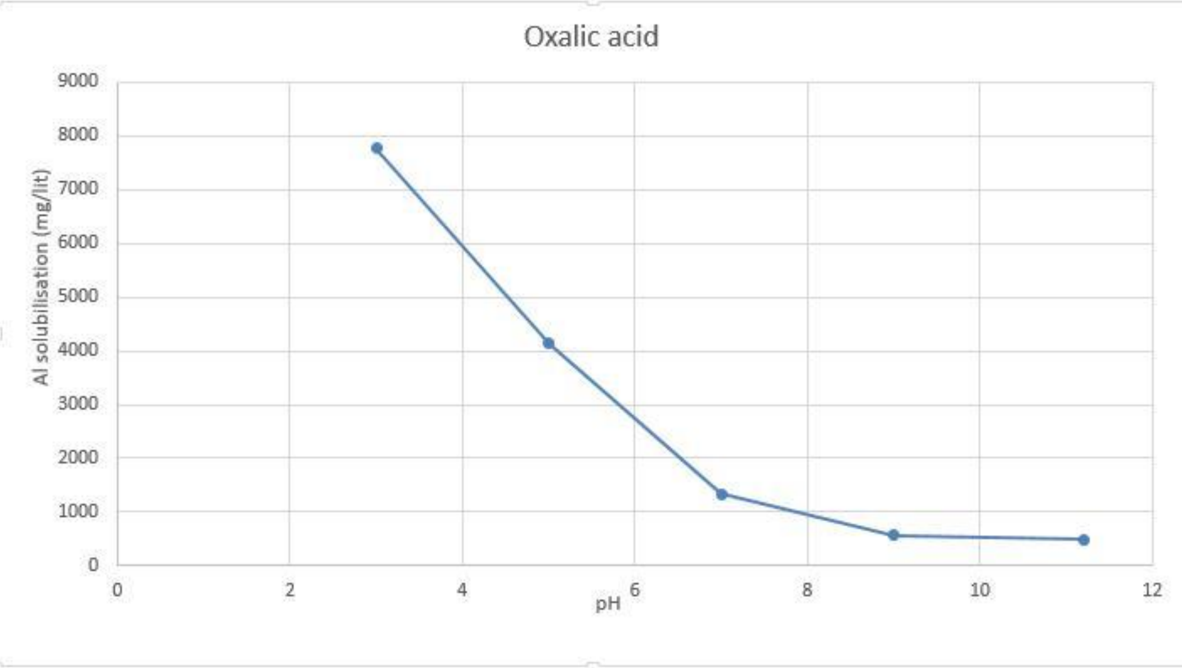

Figure 4 influence of pH on Al solibulisation by oxalic acid

Similarly using oxalic acid max 7763 mg/lit of Al could be leached at pH 3. However the amount of Al leached was reduced with increasing pH. And subsequently at around pH 9 the concentration becomes very less. The higher leaching can be justified by the fact that chelation of organic acid (oxalic acid) is more in the lower pH because of the presence of higher amount of H^+ ions.

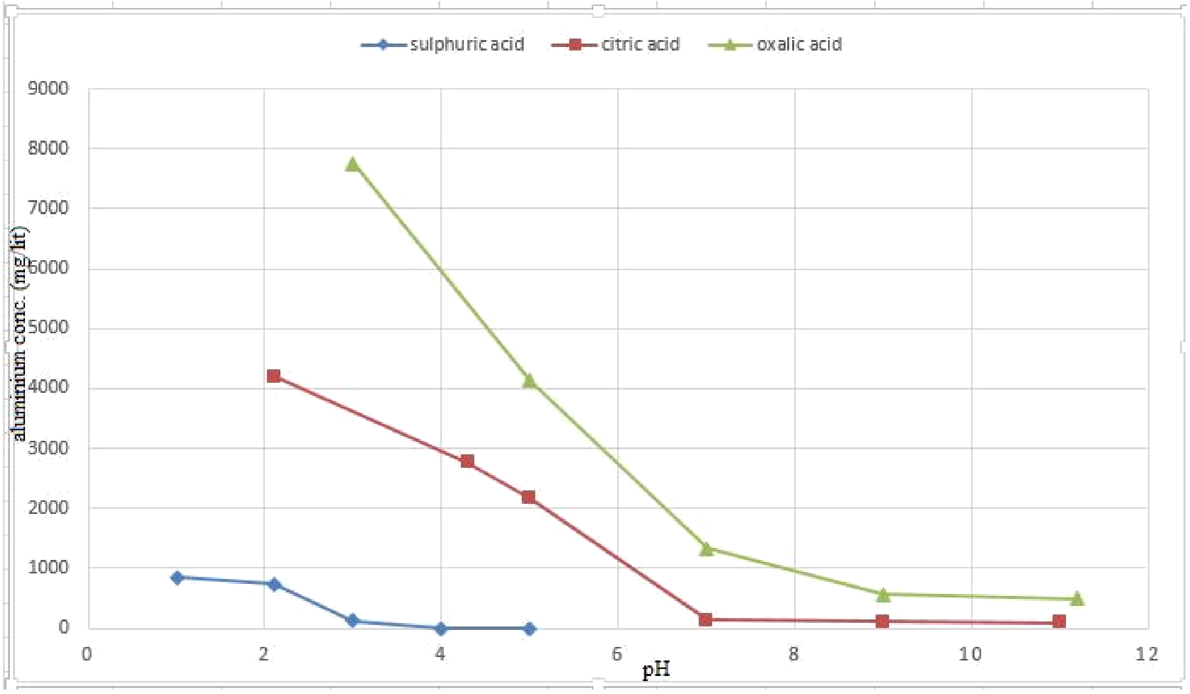

Figure 5- Influence of pH on Al solubilisation by all acids

In this figure we can clearly observe that the Al solubilisation is much more in case of organic acids then in case of inorganic acid. The higher concentration can be justified by the fact that chelation effect is more in case of organic acids. Although the protonation in case of sulphuric acid solution is more in low pH values but it is very less in comparison to chelation effect of organic acids.

<u>Table 5 - Effect of pH on Al solibulisation by combined mixture of sulphuric acid and oxalic acid.</u>

pH	Sulphuric acid(20ml)+Oxalic acid(20ml)
2	4525
3.1	3883
5	2061
7	665
9	276

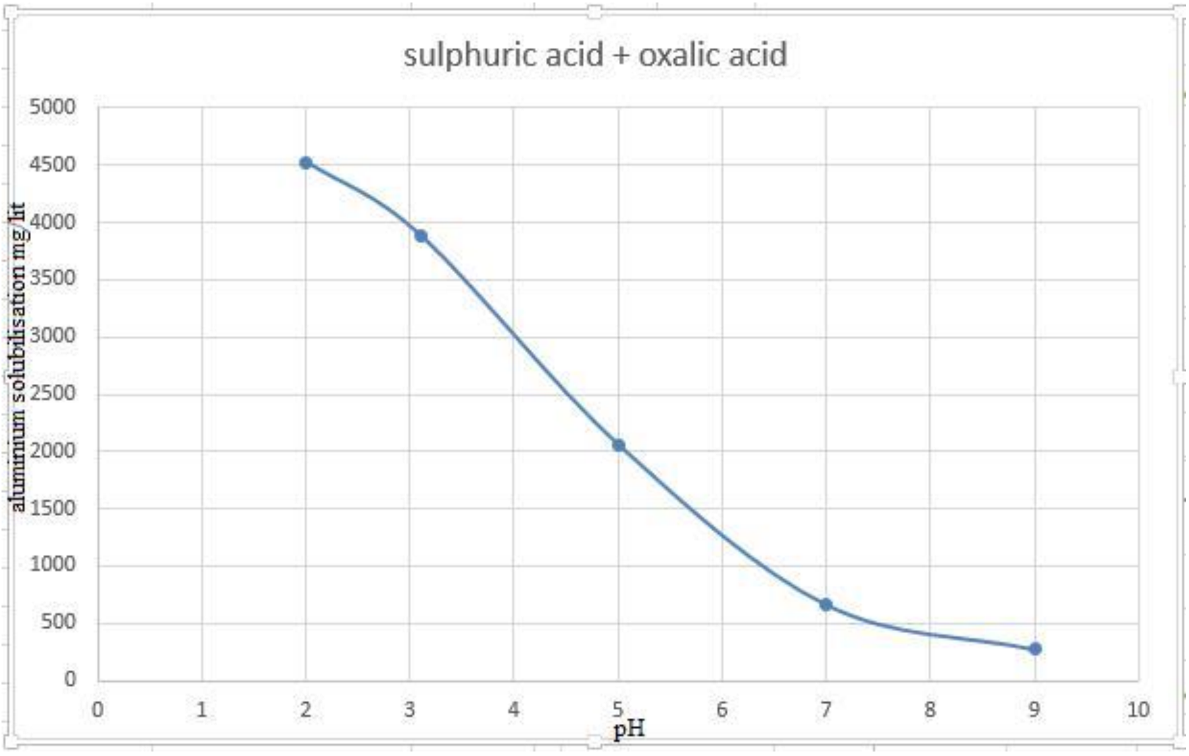

Figure 6 - Influence of pH on Al solibulisation by combined mixture of sulphuric acid and oxalic acid.

With sulphuric acid and oxalic acid mixture of 2:2 ratio pH effect was observed on acid leaching on aluminium. It din't show any improvement in the acid leaching. Rather it decreased in comparison with individual acid concentrations of citric acid and oxalic acid.

Table 6 - influence of pH on Al solibulisation by combined mixture of sulphuric acid and citric acid.

pH	Sulphuric acid(20ml) + citric acid(20ml)
3	3889
4.2	1394
5	998
7	0
9	0

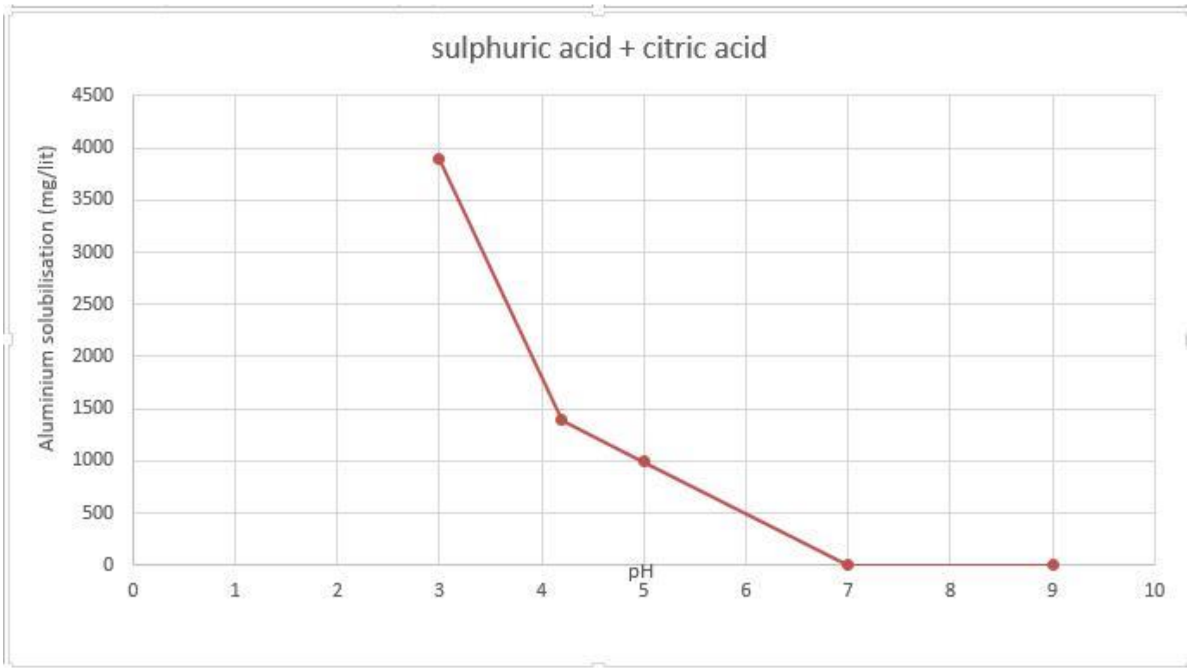

Figure 7- influence of pH on Al solibulisation by combined mixture of sulphuric acid and citric acid.

It could be observed from figure 7 that presence of sulphuric acid in the mixed acid affected the aluminium leaching. Reduction of Al leaching was observed with the presence of sulphuric acid.

Table 7 - Influence of pH on Al solibulisation by combined mixture of citric acid and oxalic acid.

pH	Citric acid (20ml) + oxalic acid (20ml)
3	8427
5	4221
7	1800
9	826
11	626

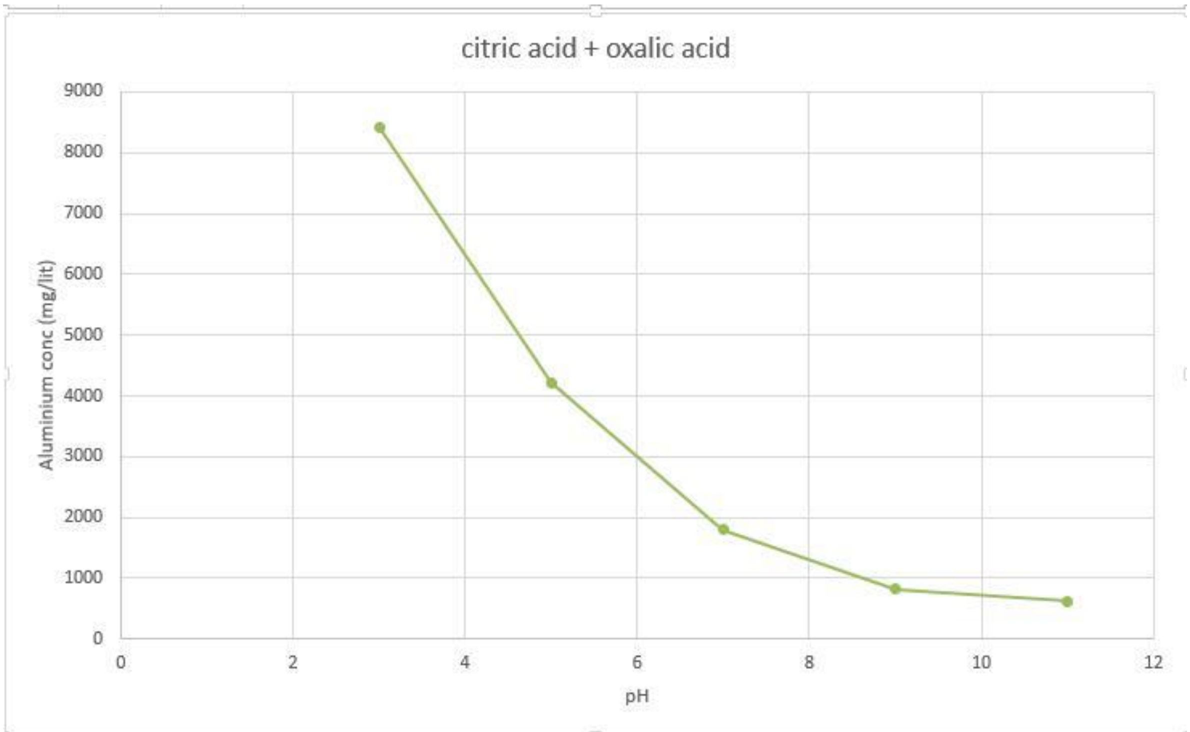

Figure 8 - influence of pH on Al solibulisation by combined mixture of citric acid and oxalic acid.

With the combination of citric and oxalic acid it was observed that the Al leaching improved significantly. The concentration of Al was more with the low pH in comparison to the higher pH.

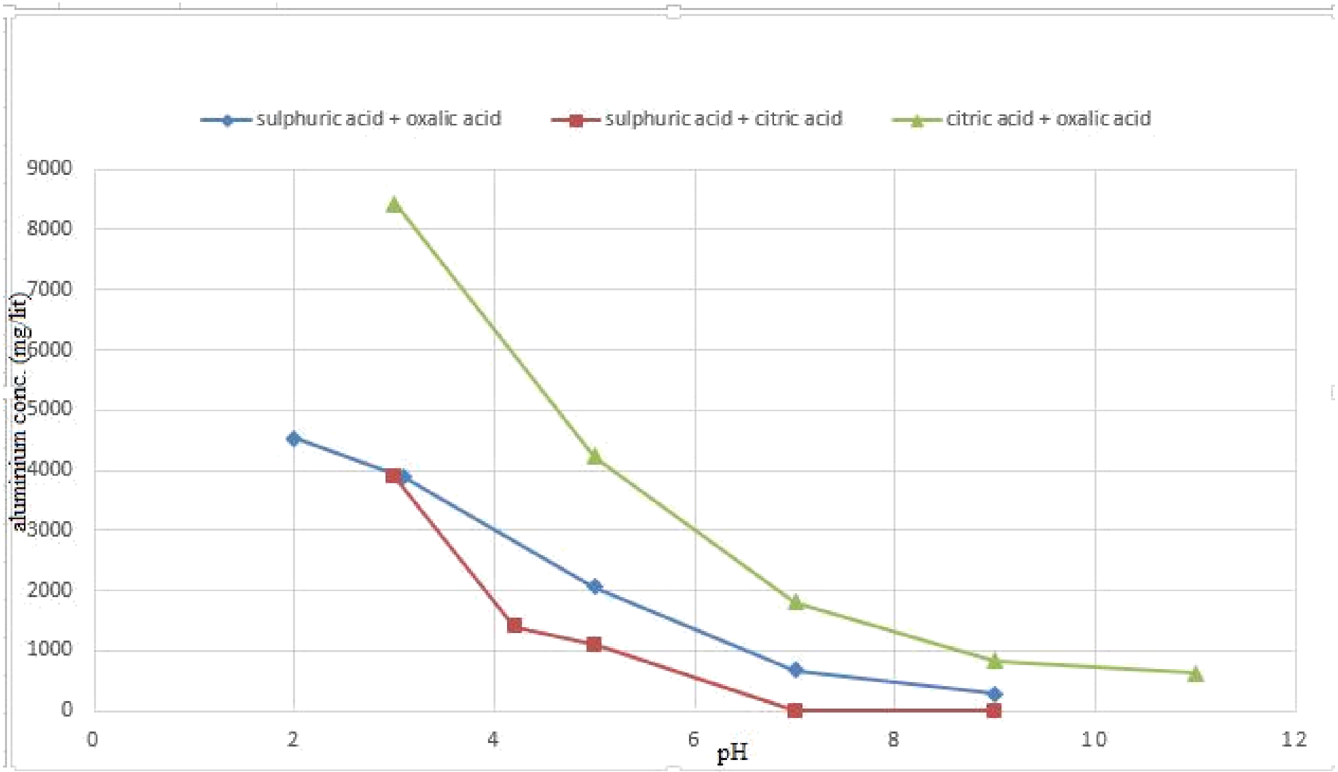

Figure 9 - influence of pH on Al solibulisation by combined mixture of citric acid and oxalic acid.

In this figure it is observed that the solubilisation of aluminium is maximum in the combination of citric acid and oxalic solution whereas it is least in sulphuric and oxalic acid solution. Because of the chelation effect by both acids in the citric acid and oxalic acid solution the solubilisation is highest in that mixture of acid solution.

Table 8 - Influence of pH on Al solibulisation by combined mixture of citric acid and oxalic acid taken in 2:1 ratio

pH	Citric acid(20ml) + Oxalic acid(10ml)
3	10924
4	4628
5	5621
7	1408
9	800
11	625

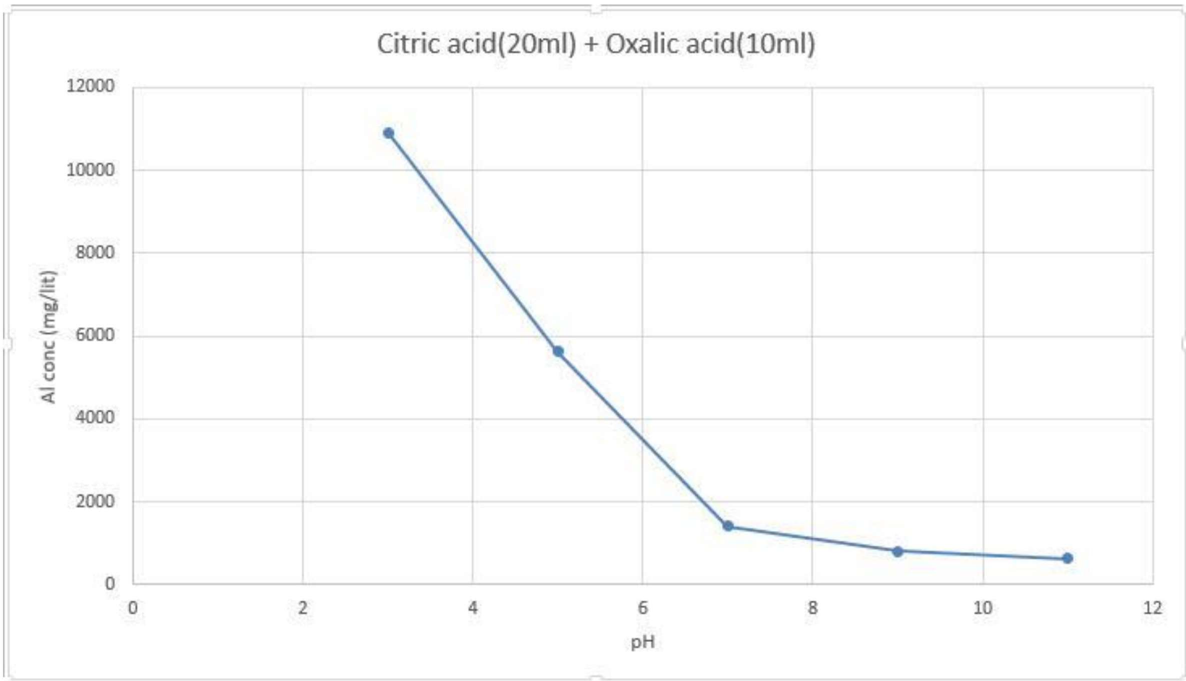

Figure 10 - influence of pH on Al solubilisation by combined mixture of citric acid and oxalic acid taken in 2:1 ratio.

It was observed that with combination of citric acid and oxalic acid at 2:1 ratio, the Al concentration increased. The maximum concentration was found to be 10924 mg/lit at pH 3.

Table 9 - influence of pH on Al solibulisation by combined mixture of citric acid and oxalic acid in 1:2 ratio.

pH	Citric acid (10ml) + oxalic acid (20ml)
3	8785
5	5128
7	1326
9	765
11	436

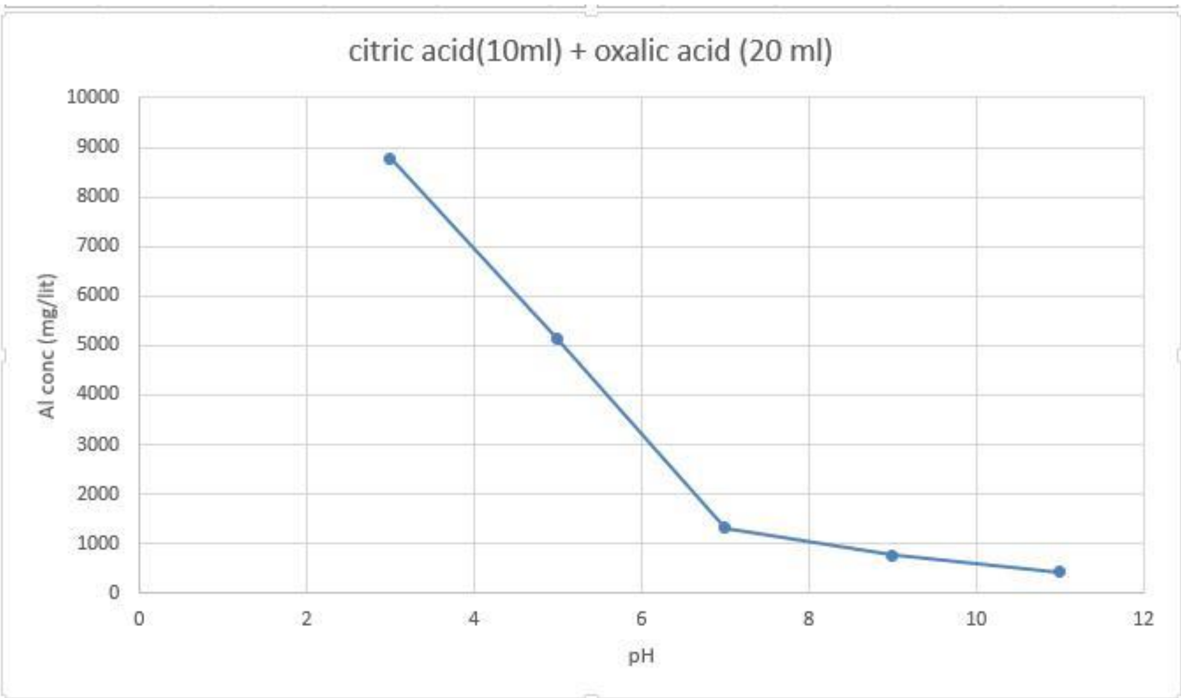

Figure 11 - influence of pH on Al solibulisation by combined mixture of citric acid and oxalic acid in 1:2 ratio.

Similarly the ratio of acid mixture was changed to 1:2 ratio and the effect of pH was observed. The max. concentration was found to be 8785 mg/lit at pH 3. However this is less than the previous ratio of acid mixture (i.e. 2:1).

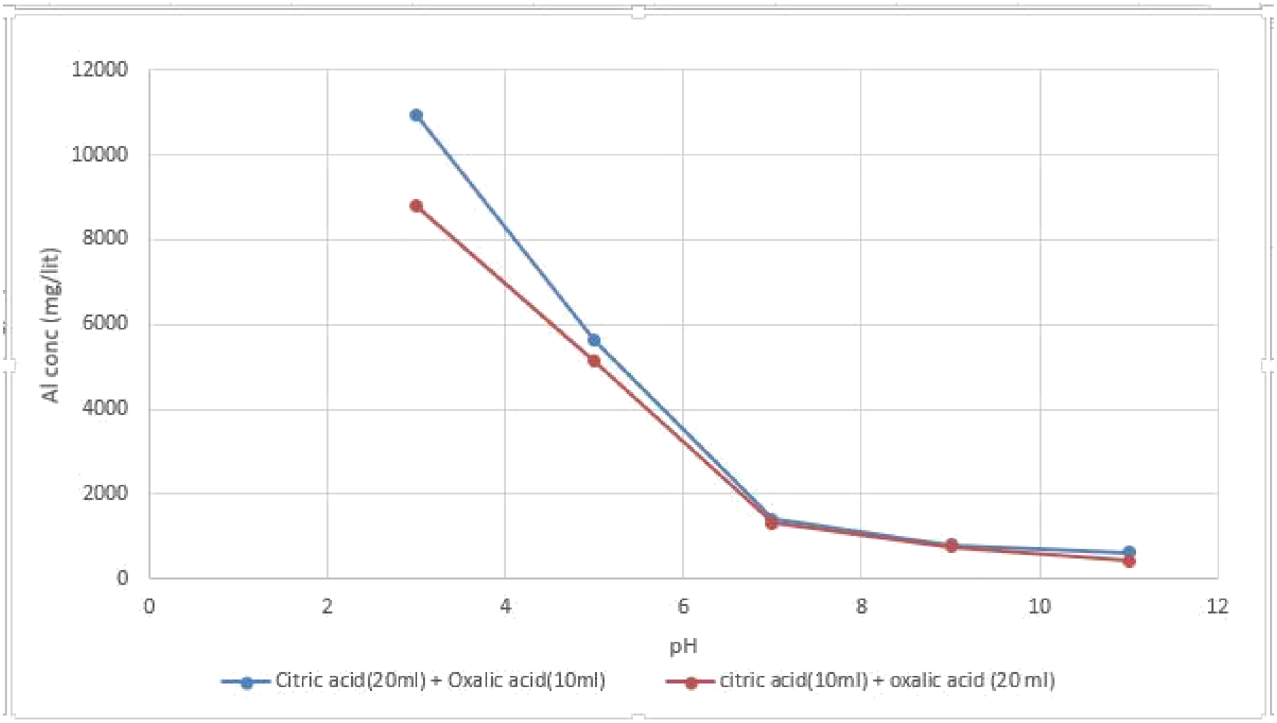

Figure 12 : the comparison of Al solubilisation with combined organic acids taken in ratio 2:1 and 1:2

The mixture of citric acid and oxalic acid in the ratio of 2:1 is solubilizing aluminium more in comparison to 1:2 ratio.

Table 10 - effect of contact time on Al solibulisation by combined mixture of citric acid and oxalic acid in 2:1 ratio.

Time(in hrs)	Citric acid (20 ml) +oxalic acid (10ml)
1	6432
3	6789
6	8534
9	8954
12	9055
18	9217
24	9146

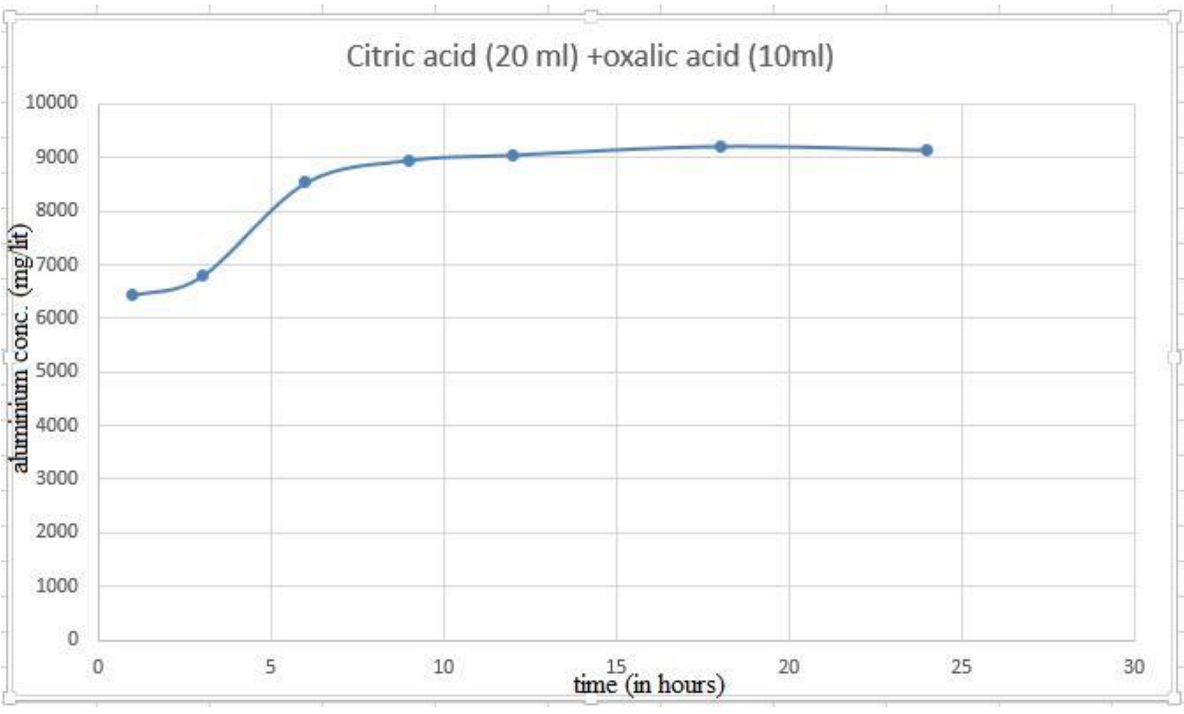

Figure 13 - influence of contact time on Al solubilisation by combined mixture of citric acid and oxalic acid in 2:1 ratio.

With increase in contact time the concentration of aluminium became steady and maximum concentration was observed after 18 hours. The Al concentration increased rapidly at the initial hours and became almost steady after 10 hours.

Table 11 - Influence of contact time on Al solubilisation by combined mixture of citric acid and oxalic acid in 1:2 ratio.

Time (in hours)	Citric acid (10ml) + oxalic acid (20ml)
1	4356
3	4468
6	6267
9	6692
12	6973
18	7489
24	7365

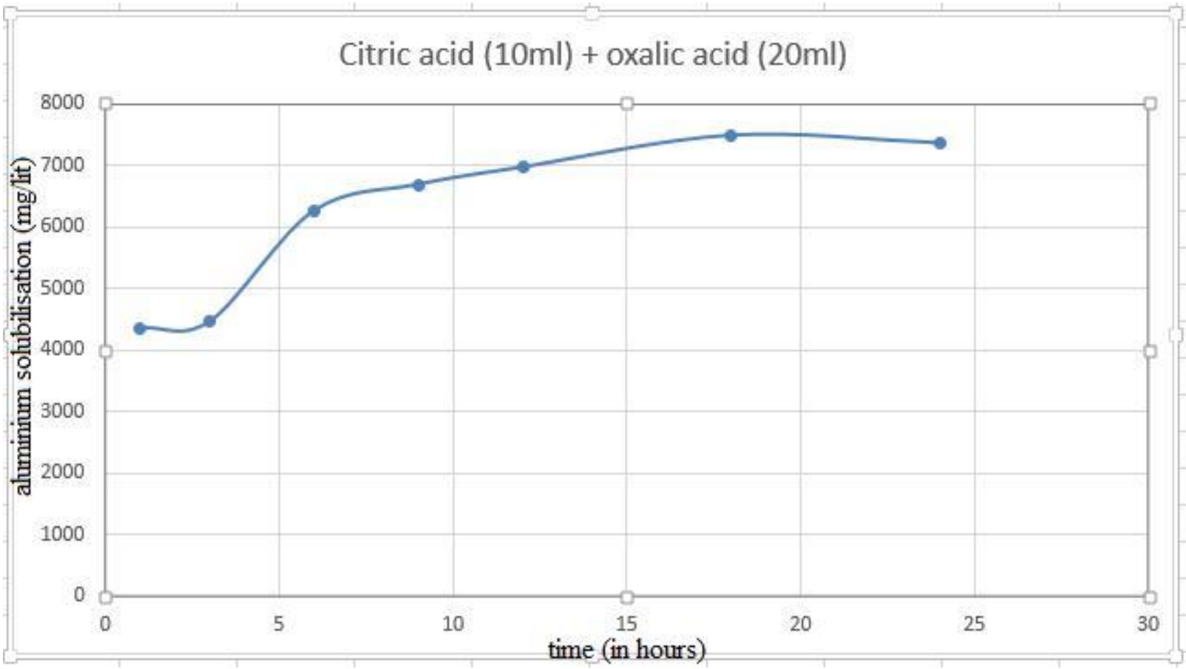

Figure 14 - influence of contact time on Al solubilisation by combined mixture of citric acid and oxalic acid in 1:2 ratio.

The effect of contact time was observed and although there is a increase in the Al concentration but the max concentration in this ratio (1:2) is lower than the previous one.

Table 12 : Influence of contact time on Al solubilisation by combined mixture of citric acid and oxalic acid in 2:2 ratio.

Time (in hours)	Citric acid (20ml) + Oxalic acid (20ml)
1	4143
3	4668
6	6976
9	7014
12	7095
18	7234
24	7427

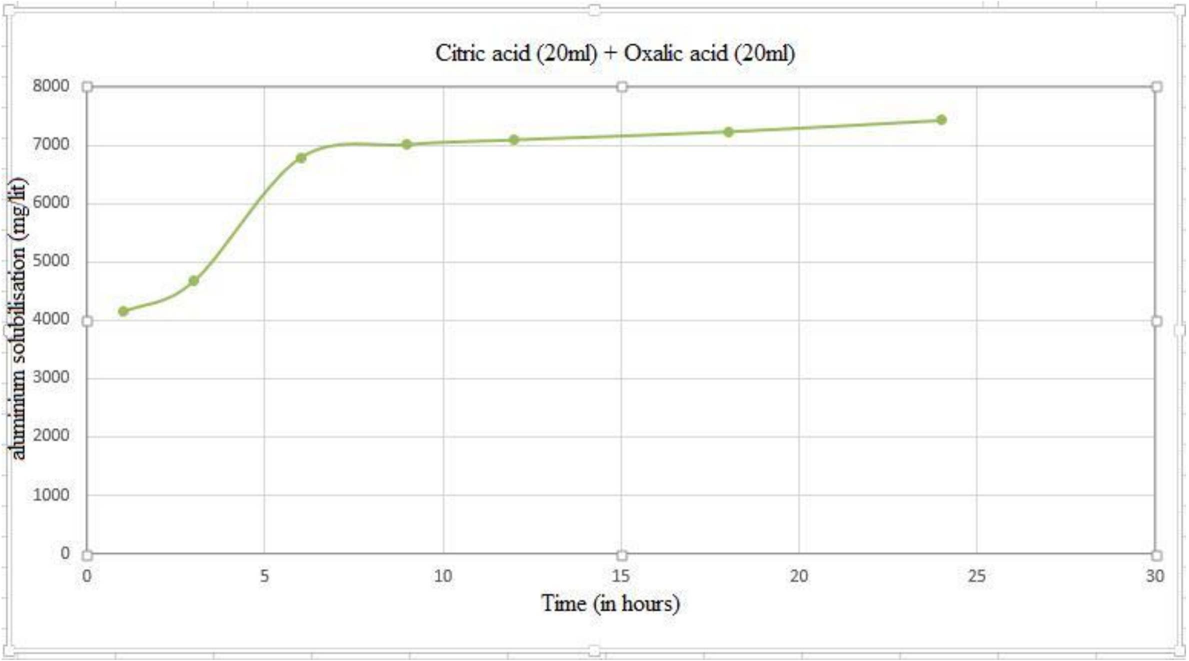

Figure 15 - influence of contact time on Al solubilisation by combined mixture of citric acid and oxalic acid in 2:2 ratio.

The effect of contact time was observed and although there is a sharp increase in the Al concentration but the max concentration in this ratio (2:2) is lower than the 2:1 ratio.

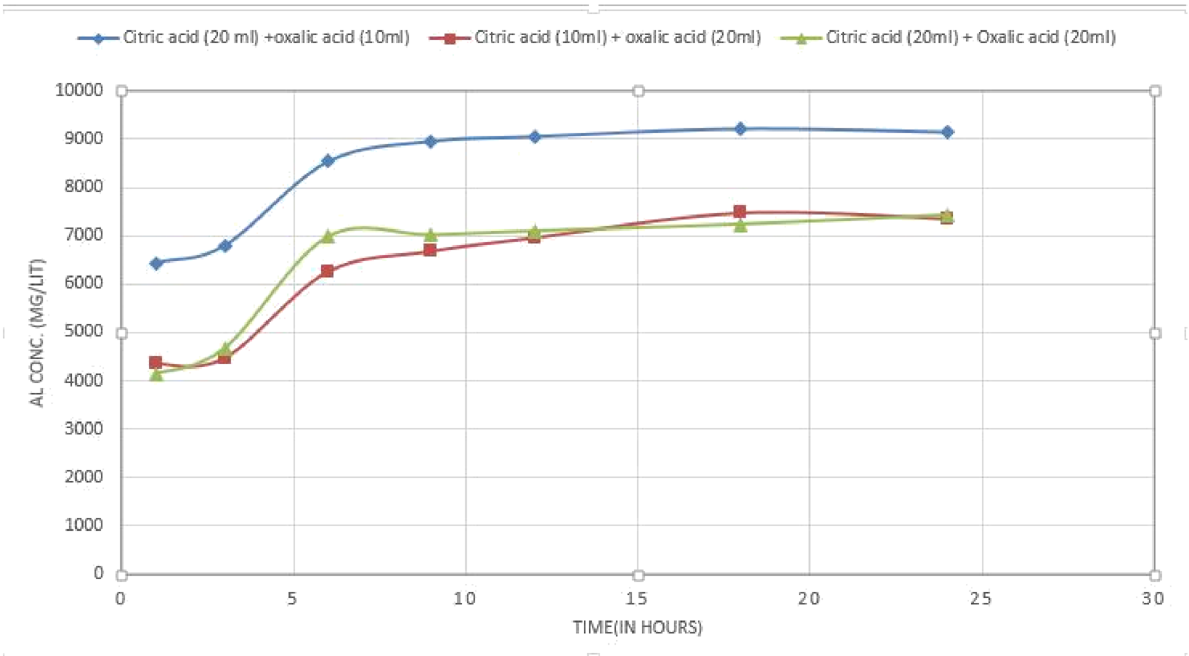

Figure 16 : Effect of contact time by the combination of organic acid mixtures taken in different ratios.

It can be observed that the Al concentration increases rapidly at the initial hours and the conc. became steady almost after 15 hours. Maximum concentration is observed after the steady state.

Table 13 – Effect of stirring rate on the aluminium solubilisation.

pH	50 rpm	100 rpm	150 rpm	200 rpm	250 rpm
3	6268	7692	9938	10924	9830
5	4016	4926	5294	5621	5582
7	951	1176	1393	1408	1635
9	557	590	674	800	933
11	368	324	456	625	605

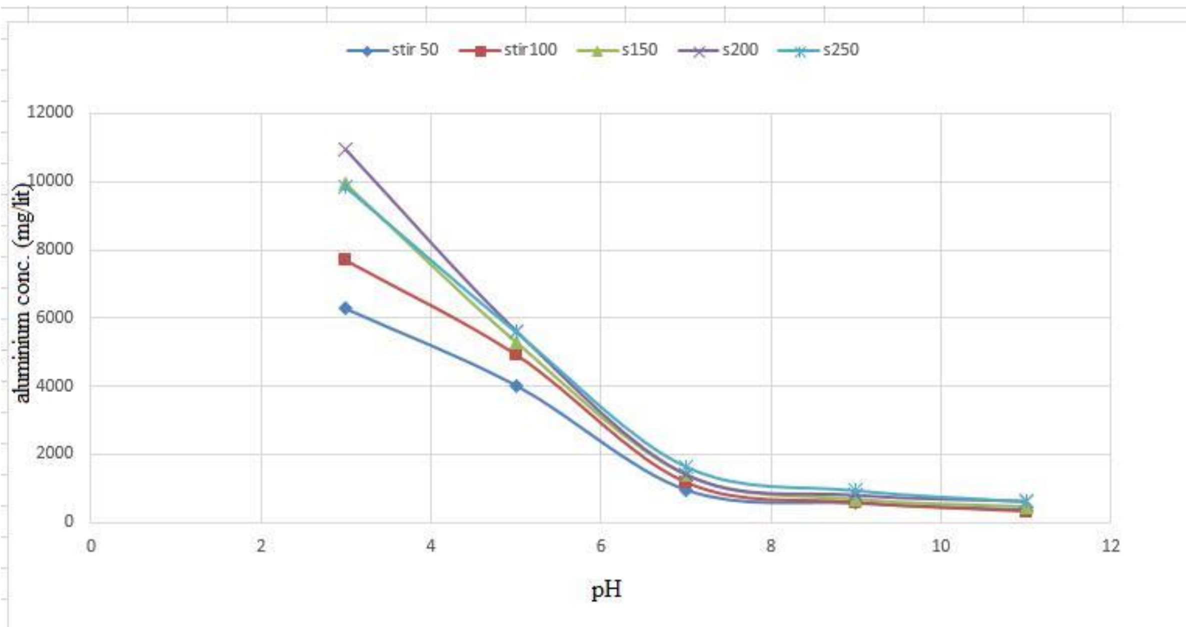

Figure 17 – effect of stirring rate on the aluminium solubilisation

Study was conducted with stirring rate of 50,100,150,200 and 250 rpm. It was observed that with increase in stirring rate the Al conc. Increased. However, the max solubilisation was found at 200 rpm.

Table 14 – effect of temperature on the aluminium solubilisation

pH	28˚C	20˚C	40˚C
3	10924	9743	9664
4	6328	6138	5676
5	5621	5287	5338
7	1408	1265	1300
9	800	754	654
11	625	576	569

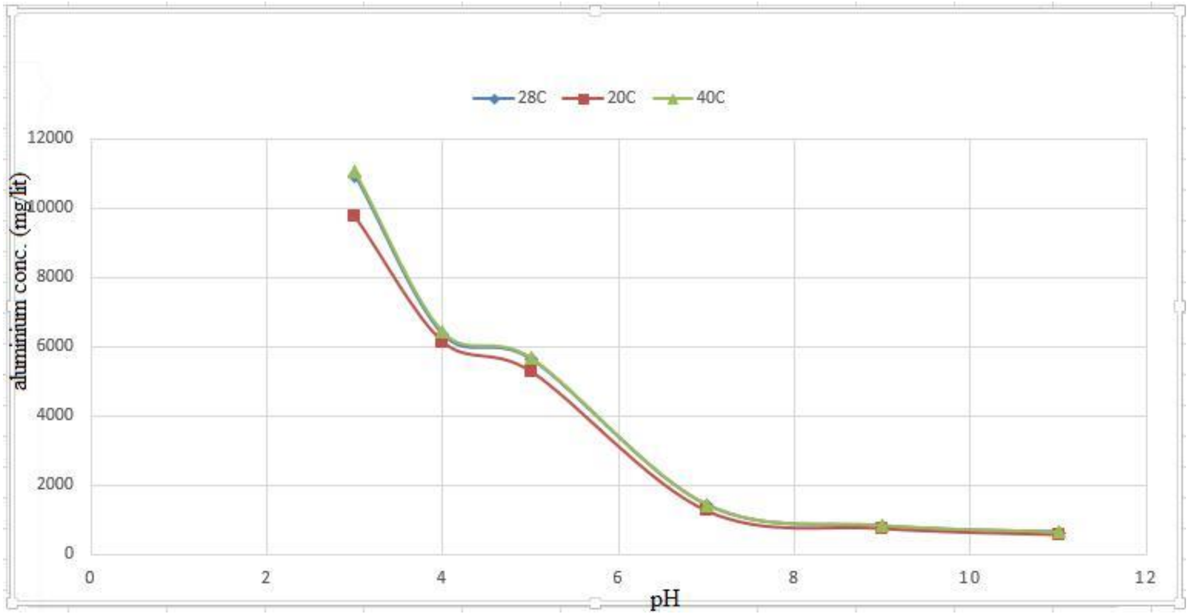

Figure 18: Effect of temperature on the aluminium solubilisation

It was observed that the concentration of Aluminium solubilisation is increasing with increase in temperature when leached with 20 ml citric acid and 10 ml oxalic acid. We have considered 28 ˚C as optimum leaching temperature as no significant leaching data is obtained at 40 ˚C with respect to aluminium leaching at 28 ˚C.

CONCLUSION

The effect of various parameters were studied such as pH, contact time, acid combination, temperature and stirring rate.

- Leaching of aluminium in the acid solution was explored and organic acids showed maximum leaching as compared to H_2SO_4 .
- With increase in pH, the leaching of aluminium decreased and optimum pH 3 was observed for organic acids.
- Influence of contact time showed that within 15 hrs of solubilisation of aluminium occurred that helped to achieve equilibrium.
- With increase in stirring rate Al leaching improved and was significant at lower pH.
- Temperature was directly proportional to leaching of aluminium. It improved from 20 ˚C to 40 ˚C. however optimum temperature 28 ˚C (room temperature) was considered as it did not show any significant change at 40 ˚C.

Thus from the present study it can be concluded that at pH 3 , temperature 28 ˚C and using 200 rpm aluminium could be leached up to 10924 mg/litres using citric acid and oxalic acid in the ratio 2:1 .

The aluminium extracted from the red mud can be reused further in the alumina industries.Although the extraction using H2SO4 was low as compared to the organic acids , still it can be used since sulphuric acid is much cheaper in comparison with oxalic acid and citric acid.

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